APPENDIX C.

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Cordierite Composites Using New Source of Waste; Sludge Cake From Aluminum Scrap and Dross Recycling Industry in Thailand

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Abstract

This study aim to synthesis cordierite composites using new source of alumina from waste. The first groups were Sludge cake from aluminum scrap and dross recycling industry (Aw.), the other groups were commercial grade Alumina and other raw materials were kaolin, ball clay and talcum. The raw materials were ground, pressed, and sintered between 1200°C to 1325°C for 1 hour. The samples were investigated by XRD and thermal shock resistance tested, firing shrinkage, water absorption, and COE. The developed of crystal were studies by SEM and EDS. The COE of the sample W. synthesized at 1325°C were 3.95 x 10^{-6}°C^{-1} and the XRD analysis present that the main crystalline phase was cordierite. It can be concluded that the Aw. is a promising raw material and beneficial to Thai ceramics industry in terms of cost saving, competitiveness and environmental.

Keywords: Sludge cake from aluminum scrap and dross recycling industry, Alumina, Waste, Cordierite

INTRODUCTION

Nowadays, as waste increases in line with growing industries, waste recycling interests both industry and academia. The practice of recycling provides environmental, economic, and social benefits i.e. recycled materials can be used again as raw materials in the same or different manufacturing processes. In ceramic industries, alumina is one of the important raw materials which can be obtained from sludge of anodizing industries [1-3]. It can be deduced that sludge from other aluminum related industries would also provide alumina. This study, then, employed sludge cake from wastewater treatment plant of aluminum scrap and dross recycling industry as alumina source.

Ceramic Industries in Thailand use imported alumina for the alumina contained in kaolin and ball-clay is not enough to impart required properties. Alumina from waste would then be beneficial to the industries in all aspects. There are about 270 aluminum recycling manufacturers in Thailand. Some of them recycle aluminum from only aluminum scrap, some from aluminum scrap and aluminum dross, and some from aluminum dross only. It is reported that every ton of aluminum recycling replaced 4-6 tons of mineral mined. Moreover, every 1 kilogram of scrap-and-dross recycled aluminum saved energy in equivalent of 7.12 litre of gasoline, in other words, energy saving of about 95% in comparison to aluminum from mining [4,5].

Wastewater treatment plant of the aluminum scrap and dross recycling industry consumed large quantity of water and generated sludge of about 20,000 tons per year [4]. The sludge was disposed of to landfill and that cost about 1,000-2,000 bath/ton (Non-hazardous industrial waste) [6]. Attaining alumina from the sludge cake is not only able, at the global level, to reduce resource depletion but also, at the local level, to reduce energy consumption, emissions, and import volume.

Cordierite ceramics are known for their high thermal shock resistance, low thermal expansion (COE as low as 0.8-2x10^{-6}°C^{-1} [7-9], low dielectric constant [10], high modulus, flexibility, and strength [11,12] which makes it desirable for many applications. It is a rare mineral with chemical formula of $2MgO{\cdot}2Al_2O_3 \cdot 5SiO_2$ (13.7% MgO, 34.9% Al_2O_3, and 51.4% SiO_2) [8,13]. The 2 different sources of raw materials were selected in this study. The first groups were commercial grade supplied by C.K. Ceramics Co. Ltd. The other groups were materials from industry wastes. The relationship between the developed cordierite phase and the different sources of materials investigated in this study will lead to future natural resources employing in thermal shock resistance ceramics in Thailand.

MATERIAL AND PROCEDURES

Alumina from two different sources was used in this study. One was Sludge cake from aluminum scrap and dross recycling industry (Aw.), another was Alumina (A-21) Sumitomo Chemical Co. Ltd., Japan. The Aw. was calcined at 700°C. Chemical compositions of the alumina from Aw. obtained from Wavelength Dispersive - X-ray Fluorescence Spectrometer (WD-XRF) (Rh type, Bruker® S4Pioneer) and x-ray diffraction pattern (Cu type, Bruker® D8Discover, 40 kV, 40 mA) were shown in Table 1 and Fig.1a, respectively. X-ray diffraction pattern of Alumina was shown in Fig.1b. Other raw materials were commercial grade supplied by C.K Ceramics Co. Ltd.: kaolin - Ranong province, Thailand; ball clay - Surajthanee province, Thailand; and talcum - Lampang province, Thailand. Compositions of each raw material are also shown in Table 1.

The Cordierite composition selected in this study was 13.7% MgO, 34.9% Al_2O_3, and 51.4% SiO_2 [10]. To obtain the composition, calculations were done according to the amount of oxides in Table 1 which resulted in weight% of each raw material as shown in Table 2. [14,15]. Aw and Alumina were used in mixtures W and C, respectively.

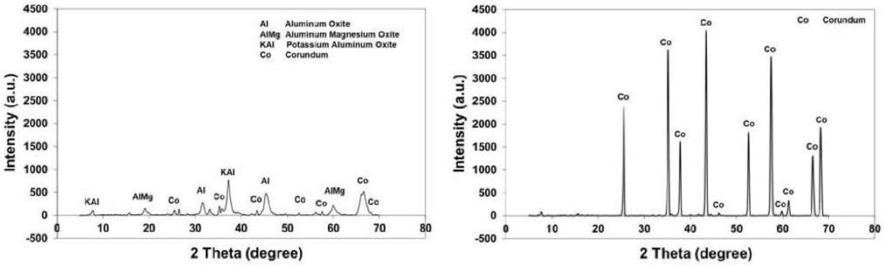
Each mixture was grinded in ball mill for 5 hours. Specimens were pressed using hydraulic compression and fired at a heating rate of 80°C/min to 1200-1325°C and soaked at the highest temperature for 1 hour. Specimens with the dimension of 5 cm x 7.5 cm x 0.7 cm were used in thermal shock resistance and water absorption tests. Specimens with the dimension 2.5 cm x 12 cm x 1 cm were used in linear shrinkage test. Physical properties of raw materials and samples were measured as follow: Particle sizes and surface area of sample were analyzed by BETTERSIZE 9300H. Thermal shock resistance, linear shrinkage, and water absorption were conducted in accordance with JIS S 2400 [16], and ASTM C373-88 (Reapproved 1999) [17], respectively. Crystal structures and their relative amount of both W and C mixtures were determined by X-ray diffraction using CuK_α radiation with a Bruker® D8 Advance Diffractometer.

Table 1: Chemical composition of raw materials. (weight %)

Oxide	Al_2O_3	SiO_2	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	ZnO	L.O.I.
Aw	78.80	5.42	1.73	4.21	1.08	-	2.68	-	1.63	-
Alumina	99.78	0.03	-	-	0.40	-	0.03	-	-	0.65
Kaolin	37.98	44.85	0.12	0.04	1.23	0.07	0.97	0.07	-	14.95
Ball Clay	23.00	51.50	0.37	0.12	0.22	0.92	1.42	0.63	-	19.60
Talcum	0.30	58.00	1.10	30.00	-	-	0.15	-	-	10.00

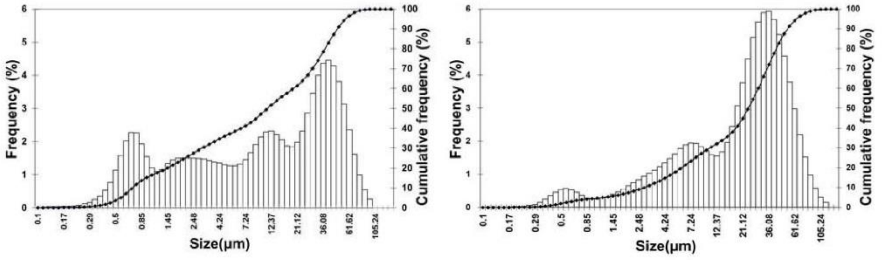
Table 2: Raw materials in weight%.

Sample no.	Aw	Alumina	Kaolin	Ball clay	Talcum
W.	21.31	-	20.74	20.74	37.22
C.	-	17.03	20.86	20.86	41.24



(a) (b)

Fig. 1: XRD pattern of the Aw (a) and Alumina Powder (b).



(a) (b)

Fig. 2: Particle size distributions of sample. (a) Aw and (b) Alumina powders.

COE was analyzed by Anter Unitherm dilatometer 1161 ranging between 25-1000 °C at a heating rate of 3°C/min. Porosity of all samples were observed after HF 0.1 % surface etching, using FEI NanoSEM 450 Field Emission Scanning Electron Microscope. Energy Dispersive Spectrometry was also employed to determine chemical compositions in the W and C samples sintered at 1350 °C.

Fig 2. displayed that the particle sizes of Aw and Alumina powders. The median particle size of Aw is 12.78 μm (D50) with surface area of 2.26m^2/g and Alumina powder is 26.5 μm (D50) with surface area of 0.99 m^2/g.

RESULTS AND DISCUSSION

Samples of all fired mixtures were passed thermal shock resistance test at 290 C.

Fig 3. displayed the linear firing shrinkage of samples W and C. at 1200-1325°C. The W-samples got higher shrinkage values than that of C-samples for all sintering temperatures. The smaller particle size of Aw. in addition to consisted of CaO, MgO, Fe_2O_3 and ZnO, functioned as flux, allowed the particles to be easily fused and better packing while sintering. The onset temperature for increasing shrinkages of both W and C mixtures was 1225 C and leveled off at 1280 C and 1250 C, respectively.

Water absorption values of samples W and C at 1200-1325°C were shown in Fig. 4. All W-samples of 1200 - 1325°C temperature range depicted lower water absorption values than those of C-samples. Same as the linear firing shrinkage, the Aw of the smaller particle size with CaO, MgO, Fe_2O_3 and ZnO compared to Alumina, could be fused at lower temperature and imparted better packing at the same sintering temperature. Moreover, the water absorption values of both samples W and C were constant from 1200°C to 1225°C.

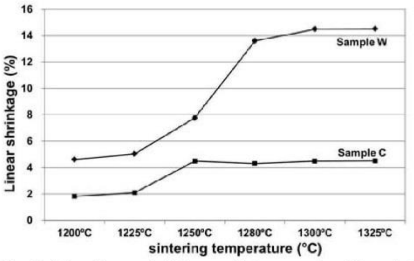


Fig. 3: The linear shrinkage of the samples W and C after firing at 1200-1325°C.

The observed values then decreased significantly at 1250°C and remained constant thereafter. The onset temperature was the same as that of the linear firing shrinkage temperature. The findings provide information of the crystalline phase transformation, which will be discussed later.

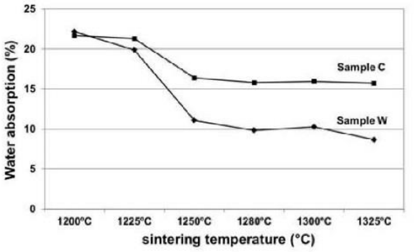
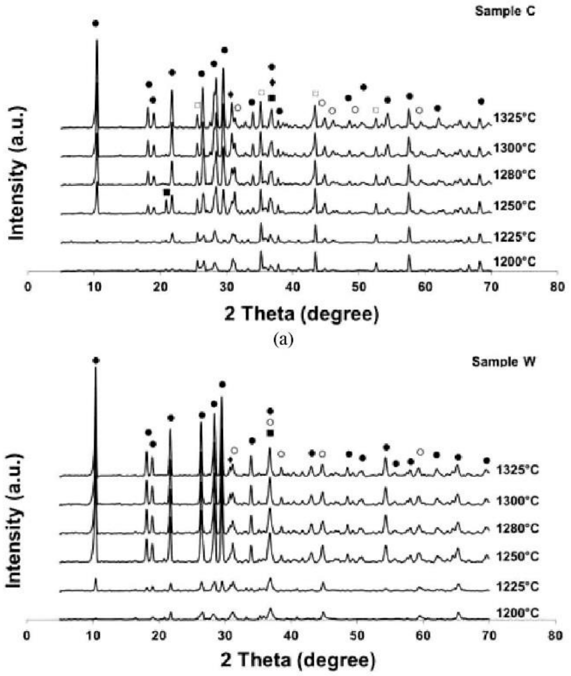


Fig. 4: The water absorption of the samples W and C after firing at 1200-1325°C.

Fig. 5 (a) and (b) showed XRD patterns of samples C and W at all sintering temperatures of 1200-1325 °C. Phase information was compiled in Table 3. At 1200°C, the sample C consists of corundum as major phase with minor phases of cristobalite, spinel, mullite, and cordierite. According to Dasgupta and Kumar [18], at this temperature, the corundum phase was formed by the reaction between intermediate phase and cristobalite or amorphous silica. These phases remained the same to 1225°C. At 1250°C, cordierite becomes major phase with minor phases of cristobalite, corundum, spinel, and mullite. As the sintering temperatures increased during 1280-1325 °C, the amount of cordierite increased whereas cristobalite disappeared from the diffraction patterns.

Sintered at 1200°C, the sample W obtains spinel as major phase and mullite, corundum and cordierite as minor phases. At 1225°C, spinel still appears as major phase with an increasing of cordierite phase. From 1250°C to 1325°C, cordierite becomes major phase and arises continuously as temperatures increase, whereas the diffracted peak intensities of spinel and mullite obviously decrease. Evidently, cordierite can be obtained in large quantity at low temperatures due to some existing active fluxing agents such as CaO, MgO, Fe_2O_3, and ZnO [19-22] at higher concentrations in both samples C and W. In addition, when compared with the sample C at the same sintering temperature, the sample W with smaller sized particles having higher surface areas and larger amount of fluxing agents tended to result in larger quantity of cordierite showing in higher proportional to the integrated area intensities obtained from the XRD patterns. Smaller particles in general can help particles pack closer during compacting, fuse easier during sintering and, hence together with the fluxing agents, synthesize more cordierite that later lowers water absorption but increases linear firing shrinkage. COE values of the W and C samples decreased with the increasing of sintering temperatures as shown in Fig. 6 The values were lower for W-sample at all temperatures. At 1225 C, the COE values of both W and C samples dropped distinctly. The COE of C-sample decreased from 8.30×10^{-6} °C^{-1} to 5.88×10^{-6} °C^{-1} as the sintering temperatures increased from 1200°C to 1280°C. The values slightly decreased thereafter and reached the value of 4.98 x 10^{-6}°C^{-1} at the sintering temperature of 1325°C.



(a)

(b)

Fig. 5: XRD patterns of samples (a) C and (b) W sintered at 1200-1325 °C. The marks are the standard peak positions of ● Cordierite, ○ Spinel, ■ Cristobalite, □ Corundum, and ♦ Mullite.

Table 3: XRD results of sintered samples at various temperatures.

Sample	Sintering temperature,(°C)	Main Phase	Other Phases	Integrated Area Intensity of Main Phase
C-1	1200°C	**Corundum**	Cristobalite, Spinel, Mullite, Cordierite	88.436
C-2	1225°C	**Corundum**	Cristobalite, Spinel, Mullite, Cordierite	81.749
C-3	1250°C	**Cordierite**	Cristobalite, Corundum, Spinel, Mullite	168.326
C-4	1280°C	**Cordierite**	Corundum, Spinel, Mullite	259.846
C-5	1300°C	**Cordierite**	Corundum, Spinel, Mullite	351.532
C-6	1325°C	**Cordierite**	Corundum, Spinel, Mullite	436.757
W-1	1200°C	**Spinel**	Mullite, Corundum, Cordierite	111.151
W-2	1225°C	**Spinel**	Mullite, Cordierite	80.088
W-3	1250°C	**Cordierite**	Spinel, Mullite	382.332
W-4	1280°C	**Cordierite**	Spinel, Mullite	390.893
W-5	1300°C	**Cordierite**	Spinel, Mullite	510.360
W-6	1325°C	**Cordierite**	Spinel, Mullite	509.205

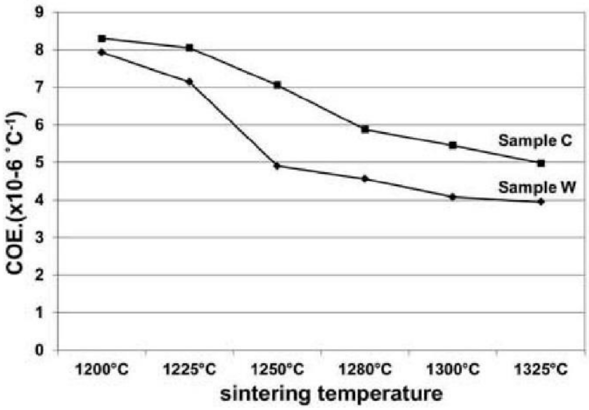


Fig. 6: COE graph of samples C and W

On the other hand, the COE values of samples W dropped distinctly during sintering temperatures of 1200°C to 1250°C from $7.35\times10^{-6}\,°C^{-1}$ to $4.89\times10^{-6}\,°C^{-1}$ and decreased very slightly to reach $3.95 \times 10^{-6}°C^{-1}$ for the highest sintering temperature of 1325°C.

It can be deduced from the results that, as the sintering temperatures increased, the COE decreased as the amount of cordierite increased and the amount of the porosity decreased. The findings seemed to be inconsistent with an equation of coefficient of thermal expansion of composite materials in that the COE had a direct relationship with the amount of cordierite and had an inverse relationship with the amount of the porosity [23-25]. However, it can be explained considering the equation:

$$\alpha_{with} = (\alpha_1 v_1 + \alpha_2 v_2 + \ldots + \alpha_n v_n)(1-P) \qquad (1)$$

Where α_1, α_2 and α_n are the thermal expansion coefficients of each raw material, v_1, v_2 and v_n are the volume fractions, and P is the porosity (equation 1.) [24]. The COE values of the each material were shown in Table 4

Table 4: The COE values of the materials [11, 12, 24, 26].

Materials	**COE. $(\times10^{-6}\,°C^{-1})$**
Cordierite	0.8 - 2.0
Mullite	4.0
Alumina	8.9 - 9.0
Spinel	8.0 - 9.0
SiC	4.0
Cristobalite	2.6

From the equation 1, the COE was proportional to the volume fraction of materials in the composite. Cordierite was one of the materials which, among all materials, possessed the smallest value of COE. The only conditions that would, then, lower the COE of the composite is an increasing of the amount of cordierite. The conditions were confirmed by the results from X-ray diffraction (Fig. 5 and Table 4) described above.

Moreover, the equation 1 also presented that the COE was inversely proportional to the amount of porosity. Fig. 4 showed that the porosity decreased as the sintering temperatures increased, should result in increasing of COE. Instead, the COE values were found to be decreased. The finding implied that the bodies taken to the vitrification point become glassy and deform [27] also the effect of porosity on the COE was surpassed by the excessive amount of cordierite which entailed decreasing of the COE.

In sample C, SEM show homogeneous structure of fused, recrystallized features and pores in the matrix, Fig.7(A.). EDS analysis and detailed microstructures of corundum cordierite and spinel are given in Fig 7 B, C and D. SEM micrographs of sample W also shows the fused, recrystallized features and pores in the matrix, Fig 8(A.). EDS analysis and SEM in Fig.8 (B.) clearly shows crystal structure of cordierite. The more detailed microstructure of cordierite and spinel are presented in, Fig 8(C and D.). Cordierite crystals clearly observed in sample W are probably due to evolution of flux contained in the body.

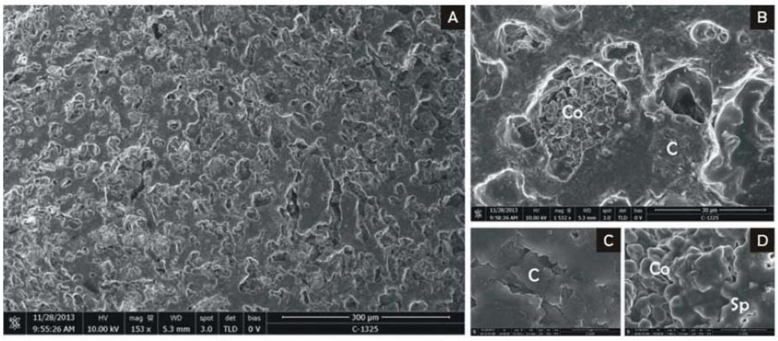


Fig. 7: SEM micrographs of samples C sintered at 1325°C (A) The etching surfaces by HF 0.1 %, (B) Crystal structure of cordierite and corundum, (C) Crystal structure of cordierite, (D) Crystal structure of corundum. (cordierite:Co, corundum:C, spinel:sp).

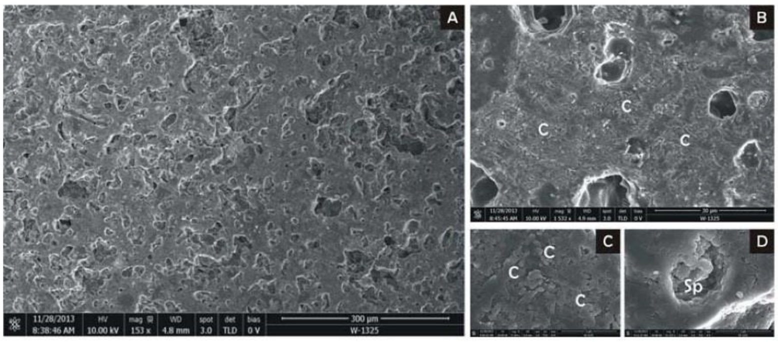


Fig. 8: SEM micrographs of samples W sintered at 1325 °C (A) The etching surfaces by HF 0.1 %, (B) Crystal structure of cordierite, (C) Crystal structure of cordierite, (D) Crystal structure of spinel. (cordierite: C, spinel: sp).

CONCLUSION

The cordierite was successfully synthesized by using alumina from sludge cake from wastewater treatment plant of old scrap as raw materials at the sintering temperature as low as 1200°C.

All fired samples were passed the thermal shock resistance test at 290°C. While the shock resistance remained the same, a higher sintering temperature caused an increase in the linear firing shrinkage and the amount of cordierite with a decrease in the water absorption and COE. A decrease of COE implied that the effect of porosity was surpassed by the amount of cordierite at the higher firing temperature.

The small particle size together with more fluxing agents of the sludge cake comparing to the calcinded alumina benefited on lower sintering temperature, more cordierite phase synthesis, and lower COE.

The results showed that the sludge cake from wastewater treatment plant of old scrap and dross industry in Thailand is a promising raw material and beneficial to Thai ceramics industry in terms of cost saving, competitiveness and environmental.

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